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Ab initio calculations on properties of low-lying electronic states of the SiF_3· radical

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A theoretical study of the electronic spectroscopy of the SiF_3 radical

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Abstract : A recent vacuum-UV fluorescence spectrum of SiF_4 (Biehl *et al.* J. Chem. Phys., 107 (1997) 720) has yielded information about the decay of electronically excited states of neutral fragments and the parent molecular cation. Emission in the visible region ($\lambda > 380$ nm) has been observed for an excitation energy of 13.0 eV with a lifetime of 3.9 ns, but the emitter was not assigned. *Ab initio* CASSCF calculations show that the observed emission is due to the $\tilde{A}\ ^2A_1 - \tilde{X}\ ^2A_1$ transition in the SiF_3 radical. The experimental lifetime, however, is too short to be attributed to this radiative process. We suggest that the lifetime is dominated by rapid internal conversion of $SiF_3\ \tilde{A}\ ^2A_1$ into high vibrational levels of the ground state.

1. Introduction

The plasma etching of silicon wafers by fluorine-containing gases (*e.g.* CF_4) is an important technological process in the fabrication of microelectronic devices. Etching proceeds by the formation of gas-phase products through ion-stimulated reaction between the wafer surface and reactive species generated by a radio-frequency discharge. The glow from such plasmas is due to emission from electronically excited species such as free radicals and molecular ions, and it is now established that the SiF_2 molecule plays an important role in the etching process [1,2]. SiF_2 has a well-established electronic spectrum, but the electronic spectroscopy of the SiF_3 radical is very poorly understood. Because no unambiguous optical sensor has been established, it is not clear if this radical plays any role in the fluorine-assisted etching of silicon.

The SiF_3 radical has pyramidal geometry, belonging to the C_{3v} symmetry point group. Despite its non-zero dipole moment, it is only recently that the microwave spectrum of this radical has been recorded [3]. All the observed transitions were *a*-type with $\Delta K_a = 0$. A unique geometry could not therefore be determined, but the *B* rotational constant was found to be 0.2505 cm^{-1}. No gas-phase infrared vibrational spectrum of SiF_3 has been reported. In the *ab initio* work reported in this Letter, we use an Si–F bond length of 1.59 Å and an F-Si-F bond angle of 108° for the electronic ground state [4] as the starting point for our calculations.

There have been three reports of emission from SiF_3 in the UV/visible electronic region of the spectrum, but none has any high-resolution content. First, a broad band (λ_{peak} = 632 nm, f.w.h.m. = 240 nm) was observed in the red region of the visible from the reaction of F atoms with a single-crystal Si sample [1,2]. Second, Suto *et al.* dispersed the emission induced from SiF_4 [5] and SiF_3H [6] , both photoexcited with fixed-wavelength vacuum-UV line sources between 90 and 100 nm. Two broad and unstructured bands, spanning the ranges 290-340 and 400-800 nm, were observed. They commented that these spectra showed some similarities with those of the CF_3 radical where discrete UV and unstructured visible bands are well characterised [7]. Third, undispersed emission in the range 380 – *ca.* 650 nm was observed by one of us when SiF_4 was excited by tunable vacuum-UV radiation from a synchrotron source [8]. This emission was only observed in the range of excitation energies 12.4-13.6 eV, with a maximum at 13.0 eV and a threshold of 12.4 ± 0.1 eV. The excited state of SiF_4 populated at 13.0 eV is either a $(3t_2)^{-1}3s$ or $(1t_1)^{-1}3p$ Rydberg state [8]. This experiment confirmed data from an earlier synchrotron study with SiF_4 by Suto *et al.* [9] who, whilst not definitively assigning the emitter, determined the fluorescence cross section of the induced emission at 13.0 eV to be 5 x 10^{-19} cm^2. Using the single-bunch, pulsed mode of the synchrotron, one of us has measured the lifetime of this visible emission to be 3.9 ± 0.7 ns [8].

In all cases, the strongest reason for assigning the visible emission band to the SiF_3 radical is not spectroscopic, but thermochemical. Using the enthalpies of formation of SiF_x determined from a guided ion beam study of Fisher *et al.* [10], the ground states of SiF_2 and SiF are calculated to lie as high as 10.08 and 16.98 eV above the ground state of SiF_4, assuming the other dissociation products are F_2 and F_2 + F, respectively. Emission down to 400 nm (or 3.1 eV) is not compatible with either species being the emitter since the threshold energy of the emission is as low as 12.4 eV. The ground state of SiF_3, however, is calculated to lie much lower at 7.18 eV above the ground state of SiF_4 [8,10], so both the UV and visible emissions observed by Suto *et al.* [5] are energetically allowed for excitation energies in the range 12.4 to 13.6 eV. Unlike CF_3 [11], however, there have been no *ab initio* calculations on the energies and radiative lifetimes of excited states of SiF_3 to confirm these assignments. This Letter reports such calculations. We show that excited states of this radical do lie at energies consistent with the observations of Suto *et al.* [5] and Biehl *et al.* [8]. However, we calculate that the radiative lifetime of the upper state of an allowed electronic transition in any region of the visible spectrum, 400-800 nm, cannot be as low as 3.9 ns.

2. Results

We compute the energies of the low-lying states of SiF_3 at the CASSCF level [12-15] in the aug-cc-pVTZ basis of Dunning [16,17]. The calculations are performed using an Si–F bond length of 1.59 Å [4]. That is, for simplicity we assume that the bond length in excited states of SiF_3 is unchanged from its ground-state value. Eight doubly-occupied core orbitals were frozen, these being the 1s orbitals of each fluorine, and the 1s, 2s and 2p orbitals of Si. A total of 8 a_1, 1 a_2 and 8 e orbitals formed the closed-shell part of the calculation, and the occupied space consisted of 11 a_1, 6 a_2 and 12 e orbitals. Figure 1 shows the variation of energy of the lowest few states of SiF_3 with respect to bond angle in the range $106^o \le \vartheta \le 120^o$. At a bond angle of 116^o, the leading configurations of the five lowest electronic states are ……. $(6e)^4(1a_2)^2(8a_1)^1$ $\widetilde{X}\ ^2A_1$, ……. $(6e)^4(1a_2)^2(9a_1)^1$ $\widetilde{A}\ ^2A_1$, ……. $(6e)^4(1a_2)^2(7e)^1$ $\widetilde{B}\ ^2E$, ……. $(6e)^4(1a_2)^2(10a_1)^1$ $\widetilde{C}\ ^2A_1$, and ……. $(6e)^4(1a_2)^2(2a_2)^1$ $\widetilde{D}\ ^2A_2$.

The observed spectroscopy is dominated by the two lowest energy states, $\widetilde{X}$ and $\widetilde{A}$, both of $^2A_1$ symmetry. The thermochemical dissociation energy of SiF_3 $\widetilde{X}\ ^2A_1$ + F lies 7.18 eV above the ground state of SiF_4 [8,10]. With the excitation energy set at 13.0 eV, the remaining 5.82 eV is partitioned between translational energy of the two photofragments and rovibronic energy of SiF_3. The only accessible electronically excited state of SiF_3 is $\widetilde{A}\ ^2A_1$, and at this energy the $\widetilde{A}\ ^2A_1$ state lies *ca.* 5.3 eV above the ground state (corresponding to a bond angle of *ca.* 115.3^o ; see Figure 1). Thus we might

expect to see an emission band extending from *ca.* 5.3 to 0.9 eV or 230-1360 nm (Table 1) ; the lower-energy threshold is determined by the smallest gap between the $\tilde{A}$ and $\tilde{X}$ states which pertains at planarity (Figure 1). The experiments of Suto *et al.* [5] and Biehl *et al.* [8] cannot detect the predicted high-wavelength region due to the insensitivity of photomultiplier tubes above *ca.* 800 nm. The predicted low-wavelength threshold of 230 nm assumes that all the excess energy after fragmentation is taken up by rovibronic energy of SiF_3, especially in the ν_2 vibrational bending mode. The observed band, however, occurs in the range 400-800 nm [5], suggesting that fragmentation of SiF_4* yields fragments with *ca.* 2 eV in translational energy or in the stretching modes of SiF_3.

The CASSCF transition moment for SiF_3 $\tilde{A}\ ^2A_1 - \tilde{X}\ ^2A_1$ varies smoothly over the range of F-Si-F bond angles pertinent to this problem, *ca.* 115° to 120° (Figure 1), with values increasing smoothly from 0.4 to 1.4 a.u. as the bond angle increases (Table 1). The radiative lifetime of SiF_3 $\tilde{A}\ ^2A_1$ corresponding to the experimentally-observed range of emission wavelengths, 400 to 800 nm, is then calculated to be in the range 80 to 190 ns. Even for emission at the predicted low-wavelength threshold of 5.3 eV or 230 nm, the lifetime is calculated to be as high as 30 ns (Table 1). These lifetimes are between 8 to 50 times greater than the experimental lifetime of 3.9 ns [8]. The radiative lifetime is inversely proportional to the cube of the energy separation between the two states, and to the square of the transition moment. We do not expect higher levels of theory to change the transition moments or the $\tilde{A} - \tilde{X}$ energy separation to any significant extent. Indeed, such theory is likely to *decrease* the energy separation between the $\tilde{A}$ and $\tilde{X}$ states for a given value of the bond angle, thereby *increasing* the calculated lifetime.

The $\tilde{A}\ ^2A_1$ state of SiF_3 must therefore be depopulated by some mechanism other than the transition observed through fluorescence in the range 400-800 nm. This alternative mechanism cannot be attributed to a UV electronic transition in SiF_3, since at the lowest wavelength at which emission is possible, 230 nm, the calculated radiative lifetime is as high as 30 ns. Furthermore, no band was observed in the spectra of Biehl *et al.* around this wavelength (see Figure 2 of reference 8). Suto *et al.* [5] *have* observed a UV spectrum in the range 290-340 nm when SiF_4 was photodissociated at an excitation energy of 13 eV. However, this band is centred at *ca.* 310 nm, and there is good evidence that this is the bound-to-free $\tilde{D}\ ^2A_1 - \tilde{A}\ ^2T_2$ transition of SiF_4^+ arising from second-order radiation at 26 eV [8].

We conclude that the visible emission observed by Suto *et al.* [5] and Biehl *et al.* [8] when SiF_4 is photoexcited at 13.0 eV is due to the $\tilde{A}\ ^2A_1 - \tilde{X}\ ^2A_1$ radiative transition of SiF_3, but the observed lifetime must be dominated by a faster, competing non-radiative process. This is similar to the situation in the $\tilde{a}\ ^3B_1$ state of SiF_2 produced in the same set of experiments by photodissociation of SiF_4 at 15.9 eV

[8], where a fast decay component of 2.6 ± 0.4 ns was measured. This was interpreted to be the lifetime for inter-system crossing from high vibrational levels of the $\tilde{a}\ ^3B_1$ state into its electronic ground state, and not the radiative lifetime of spin-forbidden $\tilde{a}\ ^3B_1 - \tilde{X}\ ^1A_1$ phosphorescence. For SiF_3 $\tilde{A}\ ^2A_1$, the most likely non-radiative process is internal conversion into high vibrational levels of the electronic ground state. We tentatively suggest that this mechanism is responsible for the low measured lifetime of SiF_3^*.

3. Conclusions

We have performed CASSCF calculations on the low-lying states of the SiF_3 radical. We conclude that fluorescence in the range 400-800 nm observed by both Suto *et al.* [5] and Biehl *et al.*[8] following fragmentation of the $(3t_2)^{-1}3s$ or $(1t_1)^{-1}3p$ Rydberg state of SiF_4 at 13.0 eV arises from the $\tilde{A}\ ^2A_1 - \tilde{X}\ ^2A_1$ transition of SiF_3. The observed lifetime of 3.9 ns is probably dominated by rapid internal conversion of SiF_3 $\tilde{A}\ ^2A_1$ into high vibrational levels of the electronic ground state. The fluorescence quantum yield of the $\tilde{A}\ ^2A_1$ state of SiF_3, defined by $k_{rad} / (k_{rad} + k_{non\text{-}rad})$ where k_{rad} and $k_{non\text{-}rad}$ are its first-order rate constants for radiative and non-radiative decay, must therefore be much less than unity.

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Table 1. Energy separation, electronic transition moment, and radiative lifetime of the upper state for the $\tilde{A}\ ^2A_1 - \tilde{X}\ ^2A_1$ transition of SiF_3 calculated at the CASSCF level as a function of the F-Si-F bond angle in the range 115° to 120°.

ϑ (F-Si-F)	ΔE / eV	λ / nm	$\lvert R_e \rvert$ / au	τ / ns
115	5.47	227	0.44	29
115.3 [a]	5.30	234	0.45	30
116	4.93	251	0.47	35
117	4.29	289	0.51	46
118	3.50	354	0.57	66
118.4 [b]	3.10	400	0.63	78
119	2.47	502	0.73	120
119.6 [c]	1.55	800	1.14	194
120	0.91	1362	1.43	615

[a] Corresponds to the bond angle at which the $\tilde{A}\ ^2A_1$ state of SiF_3 lies 13.0 eV above the ground state of SiF_4.

[b] Corresponds to the bond angle at which the separation between the $\tilde{A}\ ^2A_1$ and $\tilde{X}\ ^2A_1$ states of SiF_3 corresponds to a photon of wavelength 400 nm.

[c] Corresponds to the bond angle at which the separation between the $\tilde{A}\ ^2A_1$ and $\tilde{X}\ ^2A_1$ states of SiF_3 corresponds to a photon of wavelength 800 nm.

Figure caption

Figure 1 CASSCF energies of the lowest electronic states of SiF_3 as a function of the F-Si-F angle, ϑ, calculated with a fixed Si-F bond length of 1.59 Å. The energy scales are relative to the minimum in the $\tilde{X}\ ^2A_1$ potential curve of SiF_3 (left-hand scale) or to the ground state of SiF_4 (right-hand scale).